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*Published in:*  
Physical Review B

*DOI:*  
[10.1103/PhysRevB.69.020105](https://doi.org/10.1103/PhysRevB.69.020105)

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*Document Version*  
Publisher's PDF, also known as Version of record

*Publication date:*  
2004

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### *Citation for published version (APA):*

Sani, A., Noheda, B., Kornev, I. A., Bellaiche, L., Bouvier, P., & Kreisel, J. (2004). High-pressure phases in highly piezoelectric  $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ . *Physical Review B*, 69(2).  
<https://doi.org/10.1103/PhysRevB.69.020105>

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# High-pressure phases in highly piezoelectric $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$

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(Received 29 September 2003; revised manuscript received 1 December 2003; published 26 January 2004)

Two novel room-temperature phase transitions are observed, via synchrotron x-ray diffraction and Raman spectroscopy, in the  $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$  alloy under hydrostatic pressures up to 16 GPa. A monoclinic ( $M$ )-to-rhombohedral ( $R_1$ ) phase transition takes place around 2–3 GPa, while this  $R_1$  phase transforms into another rhombohedral phase,  $R_2$ , at  $\approx 6$ –7 GPa. First-principles calculations assign the  $R3m$  and  $R3c$  symmetry to  $R_1$  and  $R_2$ , respectively, and reveal that  $R_2$  acts as a pressure-induced structural bridge between the polar  $R3m$  and a predicted antiferrodistortive  $R\bar{3}c$  phase.

DOI: 10.1103/PhysRevB.69.020105

PACS number(s): 64.70.Kb, 77.80.Bh, 62.50.+p

$\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$  (also called PZT) solid solutions with  $x \approx 0.5$  are used, already for decades, in virtually all piezoelectric devices from ultrasound generators to micropositioners, due to their outstanding electromechanical performance.<sup>1</sup> All PZT compositions have the cubic perovskite structure at high temperatures, while they undergo a phase transition, at about 650 K, to a ferroelectric rhombohedral  $R3m$  phase (with a polarization pointing along the  $[111]$  pseudocubic direction) for Zr-rich samples and to a ferroelectric tetragonal  $P4mm$  phase (with a polarization lying along  $[001]$ ) for Ti-rich samples.<sup>1,2</sup> Recently, higher resolution synchrotron x-ray experiments at low temperatures in high quality samples have made possible the resolution of the region around the  $R3m$ - $P4mm$  boundary, and have revealed the existence of a third ferroelectric phase with a lower monoclinic ( $M$ )  $\text{Cm}$  symmetry within a narrow compositional range.<sup>3</sup> This  $M$  phase can be considered as a structural bridge between the  $R3m$  and  $P4mm$  phases since its polarization continuously rotates in the  $(\bar{1}10)$  plane from the  $[111]$  to the  $[001]$  pseudocubic directions, as the Ti content increases.<sup>4</sup> Raman measurements in PZT have also found mode splitting which are consistent with monoclinic symmetry,<sup>5,6</sup> and first-principles calculations have shown that the polarization rotation is responsible for the large piezoelectric coefficients observed in PZT.<sup>7–9</sup>

Furthermore, antiphase oxygen rotations, superimposed on polar displacements, have been recently observed within the monoclinic phase of PZT at low temperature.<sup>10,11</sup> This is consistent with first-principles calculations predicting that oxygen rotations and polar displacements are close in energy.<sup>12</sup> Interestingly, the energetical order between different phases in perovskite materials can be modified by applying an external pressure. This is clearly evidenced by earlier works observing that pressure lowers the Curie temperature of phase transitions induced by softening of zone-center phonons, such as the  $\Gamma_{15}$  polar modes in  $\text{PbTiO}_3$  (Ref. 13)—and thus leads to a cubic paraelectric phase at high enough pressure, as recently reported for  $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$  (Ref. 14)—while it increases the temperature of the transitions related to zone-boundary modes like the antiferroelectric mode

in  $\text{PbZrO}_3$ .<sup>15</sup> These opposite effects,<sup>12,13</sup> the fact that  $\text{Cm}$  is a structure bridging the  $R3m$  and  $P4mm$  phases [and is thus very sensitive to a small change of interactions (Ref. 16)], and the observed coexistence of polar displacements and oxygen rotation suggest that the phase diagram of PZT versus pressure can be extraordinarily rich.

Motivated to precisely determine and fully understand this phase diagram, we combined three complementary techniques, synchrotron x-ray diffraction, Raman spectroscopy, and first-principles calculations, to investigate  $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$  under hydrostatic pressure. These studies revealed (1) two novel phase transitions, (2) two different pressure-induced bridging structures, and (3) the absence of a high-pressure cubic paraelectric phase.

The same  $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$  ceramic pellets of Ref. 3 were used. A piece was crushed into powder and loaded in a diamond anvil cell using both nitrogen and a 4:1 methanol-ethanol mixture as pressure media for the x-ray and Raman measurements, respectively. A maximum pressure of 16 GPa was reached in hydrostatic conditions. The pressure was measured by the ruby fluorescence method.<sup>17</sup> X-ray diffraction data were taken at room temperature in the ID9 beamline at the ESRF with a monochromatic beam of  $\lambda = 0.414 \text{ \AA}$  focused to a  $30 \times 30 \mu\text{m}^2$  spot and using an angle dispersive setup with image plate detector. The unit cells for the different pressures were obtained by means of a full profile Le Bail analysis,<sup>18,19</sup> using a pseudovoigt peak shape with asymmetry correction.<sup>20</sup> A second cubic phase was used to account for the diffuse scattering found in the monoclinic phase, as in Ref. 3. Depolarized Raman spectra of the sample powders were recorded at room temperature in back-scattering geometry with a Jobin Yvon T64000 spectrometer equipped with a microscope objective and the 514.5 nm line of an Ar<sup>+</sup> ion laser as excitation line. The Raman spectra after pressure release were identical to the initial spectra attesting the reversibility of pressure-induced changes.

As shown in Fig. 1 (top), at atmospheric pressure  $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$  is just at the monoclinic-tetragonal phase transition showing a very small monoclinic distortion, with

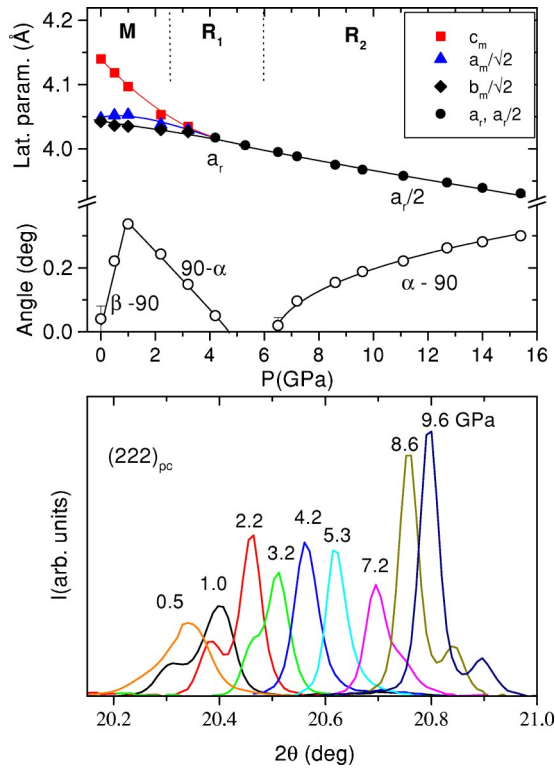


FIG. 1. (Color online) Evolution of the lattice parameters with increasing pressure (top). Solid lines are a guide to the eye. Evolution of the (222) x-ray diffraction peak with pressure (bottom).

lattice constants  $a_m$ ,  $b_m$ ,  $c_m$ , and a  $\beta$  angle. Pressure induces fairly large and continuous changes in  $c_m$ , in agreement with Ref. 14, and far more subtle changes in  $a_m$ ,  $b_m$ , and  $\beta$ . Small pressures below 2 GPa increase the monoclinic distortion by increasing both  $\beta$  and the difference between  $a_m$  and  $b_m$ . At  $\sim 2-3$  GPa,  $a_m = b_m = c_m$ , and the triplet of the pseudocubic (222) reflection [see Fig. 1 (bottom)] observed at low pressures changes into a doublet. The corresponding new phase, denoted by  $R_1$ , is rhombohedral with an angle  $\alpha < 90^\circ$ , or unit cell elongated along [111].<sup>21</sup> The most plausible space group for  $R_1$  is  $R3m$  since this latter is ferroelectric with polarization along [111]. For  $P > 3$  GPa, the rhombohedral distortion of  $R_1$  decreases with increasing pressure, until at about 5 GPa when the diffraction pattern seems to be cubic with no visible peak split in agreement with Ref. 14. However, an analysis of the peak widths shows that they are not resolution limited, suggesting local noncubic distortions. Interestingly, when the pressure is further increased, above 7 GPa, the distortion from cubic continuously increases and the diffraction peaks start splitting again. As seen in Fig. 1 (bottom), the diffraction pattern is again that of a rhombohedral phase but this time with  $\alpha > 90^\circ$ .<sup>21</sup> This new phase (denoted by  $R_2$ ) is thus associated to a unit cell flattened along [111]. One good candidate for the symmetry of  $R_2$  is  $R\bar{3}c$  since all known rhombohedral perovskites with  $\alpha > 90^\circ$  adopt this space group,<sup>22</sup> a well-known example being  $\text{LaAlO}_3$ . In this *nonpolar* structure the distortion from cubic is due to antiphase rotations of the oxygen octahedra around the [111] direction, which results from the condensa-

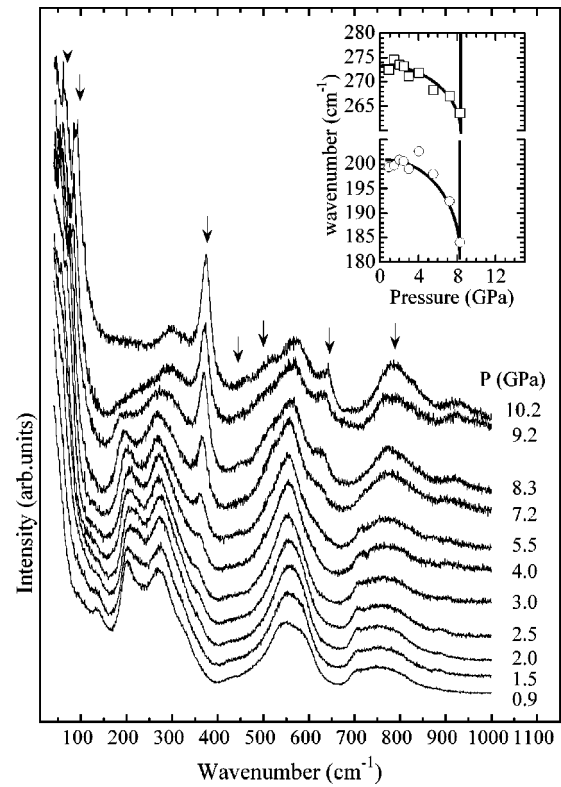


FIG. 2. Evolution of the Raman spectra with increasing pressure. Arrows mark new reflections in the high-pressure phase. The inset shows the softening of the modes at 200 and 280  $\text{cm}^{-1}$  at the  $R_1$ - $R_2$  phase transition.

tion of zone-boundary modes ( $R_{25}$ ) and thus double the unit cell.<sup>23</sup> This type of rotations is also observed in Zr-rich PZT at atmospheric pressure and low temperature, although in this case polar displacements are also present and the structure has the space group  $R3c$  with  $\alpha < 90^\circ$ .<sup>24</sup>

Raman measurements were performed to complement the x-ray data. Figure 2 presents the evolution of the Raman spectra of the same sample with increasing pressure until 10.2 GPa. A particularly striking finding is that the Raman signal is fairly well defined for any pressure, including those around 5–7 GPa for which x ray shows a cubic-like structure, implying the existence of noncubic distortions on the Raman characteristic length scale (about 5–10 unit cells), too small for x rays to resolve it. Furthermore, the spectra at low pressures are similar to those reported in the recent literature<sup>5,6,14</sup> for similar compositions. Several changes are noted upon increasing pressure. The most obvious one being the appearance of several new bands at high pressures (marked with arrows in the figure) and the suppression of some others. Most of the changes appear in between 5.5 and 7.2 GPa, in agreement with the critical pressure observed by x-ray diffraction for the transition to the  $R_2$  phase. The strong and sharp band at 380  $\text{cm}^{-1}$  has been observed under pressure in other perovskites and has been associated with rhombohedral symmetry.<sup>25,26</sup> Its narrow width at high pressures is indicative of the long-range character of the distortion, and the increase in the number of bands is also consistent with a doubling of the unit cell. Furthermore, we

observe a softening of the two modes in the 200-to-350  $\text{cm}^{-1}$  range (inset Fig. 2), accompanied by a progressive disappearing of the 200  $\text{cm}^{-1}$  mode, both observations clearly supporting the occurrence of a phase transition, most possibly related to fundamental changes of the Zr/Ti-cation displacement.

In order to gain further insights, we also perform 0 K calculations within the local-density approximation (LDA),<sup>27</sup> using the virtual crystal approximation (VCA) proposed in Ref. 28 (in which further details of the calculations can be found). We limit ourselves to the study of seven phases: the *paraelectric* cubic Pm-3m state; the *ferroelectric* monoclinic Cm, rhombohedral R3m, and tetragonal P4mm phases; the *antiferrodistortive* rhombohedral  $\bar{R}3c$  and tetragonal I4/mcm phases; and the rhombohedral R3c state that can exhibit *both* polar and antiferrodistortive degrees of freedom. The lattice vectors of the Cm, R3m, and P4mm phases are those experimentally determined in Refs. 29 and 30 for an atmospheric pressure, and the associated strain tensors—with respect to the cubic case—are kept frozen in our calculations. On the other hand, for computational convenience, the lattice vectors of the  $\bar{R}3c$ , I4/mcm, and R3c phases do not contain any strain with respect to the cubic phase. Figure 3(a) shows the  $\Delta H = H - H_{\text{cubic}}$  difference between the enthalpy of each phase and the  $H_{\text{cubic}}$  enthalpy of the cubic paraelectric phase as a function of pressure. It is well known that LDA usually underestimates the lattice constant, which explains why the LDA-predicted pressure corresponding to the experimental volume determined in Ref. 29 for the Cm phase, at low temperature and at an atmospheric pressure, is found to be  $-8$  GPa. Therefore, in order to compare with the experiments, we have performed a uniform shift of the theoretical  $P$  scale by 8 GPa, as indicated in Fig. 3 by the *rescaled* theoretical pressure  $\bar{P}$ .

One can note that our simulations yield a R3m phase that is slightly more favorable than Cm for  $\bar{P}=0$ . This discrepancy between theory and experiments for the ground-state symmetry is likely due to the fact that we neglect an important feature of monoclinic phases in our VCA calculations, namely the significant disorder existing between local dipoles located in different five-atom cells.<sup>31,32</sup> On the other hand, further using this rescaled pressure scale leads to a R3m-R3c transition occurring around 6 GPa. This is in remarkable agreement with the experimentally determined  $R_1$ - $R_2$  transition pressures mentioned above,<sup>33</sup> and thus strongly suggests that the spaces groups of  $R_1$  and  $R_2$  are R3m and R3c, respectively. The calculations further predict that R3c transforms into a  $\bar{R}3c$  phase for pressure  $\bar{P}$  around 20 GPa. (Note that  $\Delta H$  of the R3c and  $\bar{R}3c$  phases are quite negative even for  $\bar{P}$  larger than 20 GPa, which further confirms the *absence* of a high-pressure cubic phase.)

Figures 3(b) and 3(c) show the pressure behavior of the local soft-mode  $\mathbf{u}$  (directly related to the spontaneous polarization<sup>34</sup>) and the rotation angle of the oxygen octahedra, respectively, for the relevant phases. One can clearly see that the  $z$  coordinate of  $\mathbf{u}$  in the Cm phase significantly decreases when increasing  $\bar{P}$  from 0 to 2 GPa, while the cor-

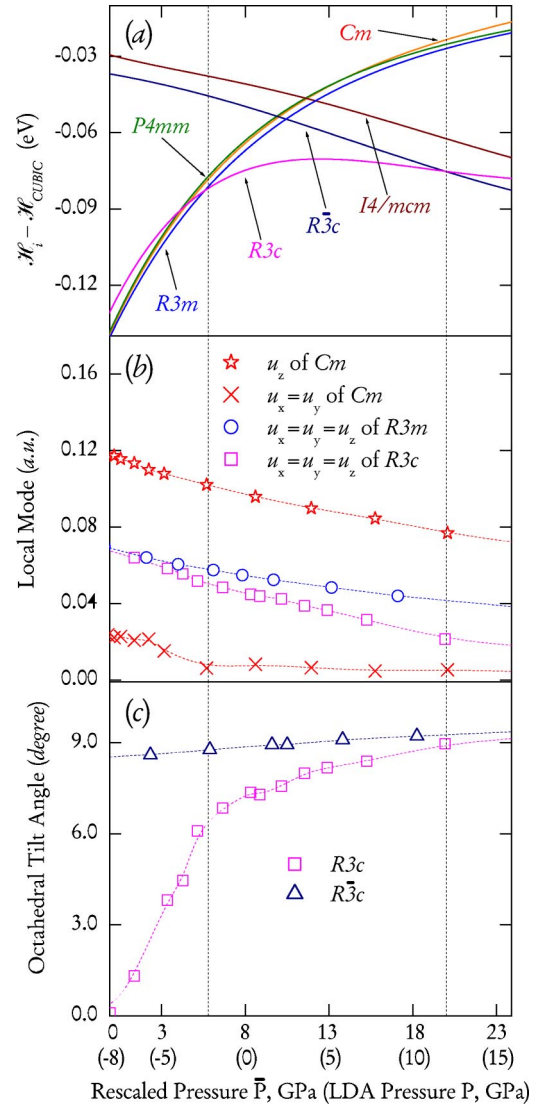


FIG. 3. (Color online) First-principles prediction of the pressure behavior of (a)  $\Delta H$  (see text) for all the considered phases (the phase corresponding to a minimal  $\Delta H$  at a given  $P$  is thus the most stable one for this pressure), (b) the polar local soft mode for the Cm, R3m, and R3c phases, and (c) the rotation angle of the oxygen octahedra with respect to the pseudocubic [111] direction for the R3c and  $\bar{R}3c$  phases.  $\bar{P}$  is the rescaled pressure (see text). LDA-pressure  $P$  is indicated in parentheses.

responding  $x$  and  $y$  components are barely affected by this change of pressure. (Note that the  $x$ ,  $y$  and  $z$  axes are chosen along the pseudocubic [100], [010], and [001] directions, respectively.) These predicted behaviors are consistent with the pressure changes of  $a_m$ ,  $b_m$ , and  $c_m$  depicted in Fig. 1 for the  $M$  phase, since ferroelectrics are well known to exhibit a coupling between polarization (related to  $\mathbf{u}$ ) and strain (related to lattice vectors).<sup>34</sup> Similarly, the continuous decrease predicted for every component of  $\mathbf{u}$  in the R3m phase—when increasing  $\bar{P}$  from 2 to 6 GPa—is consistent with the experimentally observed increase (see Fig. 1) towards  $90^\circ$  for the rhombohedral angle of  $R_1$  in this range. Figures 3(b) and 3(c) further indicate that in the R3c phase for rescaled pres-



tures above 3 GPa, the spontaneous polarization decreases in magnitude while the rotation of the oxygen octahedra increases, at increasing pressure. First-principles calculations thus provide a successful explanation for the unusual phase that is Raman active but characterized by a  $\alpha$  angle  $\approx 90^\circ$  between its lattice vectors, and that is observed for pressure ranging between 5 and 7 GPa (see Figs. 1 and 2): this phase is simply a R3c structure in which polar displacements (favoring  $\alpha < 90^\circ$ ) compete with the rotation of the oxygen octahedra (favoring  $\alpha > 90^\circ$ ). When further increasing pressure, the simulations yield a significant increase (decrease) of the antiferrodistortive (polar) structural features. This explains why  $\alpha$  increases with pressure after 7 GPa (see Fig. 1), and also indicates that R3c behaves as a pressure-induced bridging structure between the R3m and  $\bar{R}3c$  phases (which are not in a simple supergroup or subgroup relation).

In summary, complementary synchrotron x-ray diffraction, Raman spectroscopy, and first-principles calculations in piezoelectric  $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ , under pressure, reveal two novel room-temperature phase transitions. The first transition occurs around 2–3 GPa from the ferroelectric monoclinic Cm phase to a ferroelectric rhombohedral R3m phase. The second transition occurs at  $\sim 6$ –7 GPa, from the ferroelectric rhombohedral R3m phase to a rhombohedral R3c phase exhibiting both polar and antiferrodistortive structural fea-

tures. The first transition thus involves polarization rotation, while the second transition leads to a smooth suppression of the polar displacements and continuously increases the oxygen rotations around the Zr/Ti cations with increasing pressure. The pressure phase diagram of PZT thus contains two peculiar bridging structures: polar Cm that can be seen as the natural evolution of polar P4mm to polar R3m, and R3c that brings polar R3m to antiferrodistortive  $\bar{R}3c$ . The absence of a high-pressure cubic phase is, therefore, reported. Our results may also be relevant to thin films because of the crucial role played by the stress in these two-dimensional systems. Finally, we would like to raise the possibility that the mysterious (cubiclike while polar) so-called x phase, recently reported in some complex perovskites,<sup>35</sup> is a phase similar to the one we observe at the R3m-R3c transition, namely a phase in which polar distortions compete with antiphase oxygen rotations.

We would like to thank R. Guo and the late S.K. Eagle Park for the excellent samples and D.E. Cox and G. Shirane for very useful discussions. The theoretical part of this work is supported by Office of Naval Research Grants Nos. N00014-01-1-0600 and N00014-01-1-0365 (Center for Piezoelectrics by Design), and National Science Foundation Grant No. DMR-9983678.

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